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(54) Vinylidene Chloride Copolmer and Ethylene-Vinyl Acetate Copolymer Film and Method for Making the same

(57) Vinylidene chloride copolymer is blended with an ethylene vinyl acetate (EVA) copolymer having from about 5 to about 18% vinyl acetate content and a melt flow of from about 0.1 to about 1.0 decigram per minute and formed into a film. The presence of the EVA copolymer improves the film processing properties of the vinylidene chloride copolymer, particularly when the latter is an emulsion polymer rather than a suspension polymer. The film of the invention is useful inter alia for packing foodstuffs.

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SPECIFICATION

Polyvinylidene Chloride and Ethylene Vinyl Acetate Film and Method for Making the Same

The invention relates to a method of forming a film and the film produced by the method. In addition, the invention relates to a bag fabricated from the film.

Generally, polymers and copolymers of vinylidene chloride have found wide use as films and film layers in multilayer films in connection with packaging foodstuffs and other objects. Polyvinylidene chloride copolymer is known in the art by the term "saran" and is particularly relied upon as an oxygen barrier for preserving foodstuffs.

One typical prior art use of a film incorporating a layer of polyvinylidene chloride copolymer is for the protection and storage of primal and subprimal fresh red meat cut. One known multilayer film including polyvinylidene chloride copolymer has outer layers of ethylene vinyl acetate copolymer and a core layer of vinylidene chloride copolymer and is fabricated into a bag. The bag is heat-shrinkable. Typically, a meat cut is placed inside the bag, the bag is evacuated and clipped closed, and then the bag is heat-shrunk to form a strong airtight package. Such a multilayer film is described in Canadian Patent No. 982,923.

Generally, it is known that polyvinylidene chloride copolymer can be produced by either emulsion or suspension polymerization. The suspension method as compared to the emulsion method usually produces a resin which is more stable and possesses a narrower particle size distribution for good free flow properties, and has less inherent contamination. The resins produced by the suspension method, however, are costly as compared to the emulsion resins so that for commercial production it is preferable to use emulsion resins from an economic point of view.

Both suspension and emulsion resins present problems during the commercial production of films because polyvinylidene chloride copolymers can be degraded by elevated temperatures. For this reason, it is a common practice in the art to blend polyvinylidene chloride copolymers with stabilizers, plasticizers, and lubricants to improve the commercial extrusion of polyvinylidene chloride copolymers.

Generally, the extrusion of a polyvinylidene chloride copolymer produced by the emulsion method has the following drawbacks in connection with its use in forming a film:

1) A relatively large number of black particles appear in the extrudate and the continuous appearance of these particles frequently breaks the biorientation bubble.

2) A periodic slough-off of off-colored extrudate occurs and this results in appearance defects in the film being produced as well as breaks in the biorientation bubble.

3) The resin flow in the hopper for the extrusion screw is uneven.

4) Non-cyclic pressure pulsations occur in the extruder and these cause pulsations in the output rate and unstable conditions along the extruder screw.

The instant invention overcomes these problems and teaches the step of mixing, for example, polyvinylidene chloride copolymer produced by the emulsion method with appropriate stabilizers, plasticizers, and lubricant along with a selected ethylene vinyl acetate copolymer. When this mixture is extruded, for example, as a core layer of a multilayer film having outer layers of ethylene vinyl acetate copolymers, the following surprising results occur.

(1) The number of black particles in the extrudate is decreased along with the number of biorientation bubble breaks.

(2) The extruder head pressure fluctuations are reduced or eliminated and this indicates a more stable melt condition.

(3) A greater output per extruder screw revolution ratio occurs.

(4) Most film properties do not show a substantial change as compared to a multilayer film having a core layer without the added ethylene vinyl acetate copolymer.

(5) The oxygen permeability rate of the multilayer film remains almost unchanged or increases slightly.

(6) The adhesion between the film layers is improved.

The invention can be used in connection with polyvinylidene chloride copolymer produced by the emulsion or suspension method as well as combinations of the emulsion and suspension resins.

One embodiment of the instant invention is a film comprising from about 60% to about 95% by weight of a polyvinylidene chloride copolymer and from about 5% to about 40% by weight of an ethylene vinyl acetate copolymer containing from about 5% to about 18% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigrams per minute. Preferably, the ethylene vinyl acetate copolymer contains from about 5% to about 15% by weight vinyl acetate to provide a more acceptable oxygen transmission barrier and for economical production.

Another embodiment of the invention is the aforementioned film wherein the polyvinylidene chloride copolymer is from about 80% to about 95% by weight and the ethylene vinyl acetate copolymer is from about 5% to about 20% by weight and contains from about 5% to about 15% by weight vinyl acetate so that the total oxygen transmission at room temperature of the film is less than about 3 cubic centimeter per 100 square inches-24 hours-atmosphere.

A further embodiment of the invention is the aforementioned film wherein the polyvinylidene chloride copolymer is about 90% by weight and the ethylene vinyl acetate copolymer is about 10% by weight and contains from about 5% to about 18% by weight vinyl acetate so that the total oxygen transmission at room temperature of the film is about 2.3 cubic centimeter per 100 square inches-24 hours-atmosphere. This embodiment is particularly suited for film production using ethylene vinyl acetate copolymers which may have variable amounts of vinyl acetate content.

Yet a further embodiment of the invention is the aforementioned film wherein the ethylene vinyl acetate copolymer contains about 12% vinyl acetate so that the total oxygen transmission at room temperature is about 2.4 cubic centimeter per 100 square inches-24 hours-atmosphere. This embodiment is particularly suited for film production in which the amount of the ethylene vinyl acetate copolymer being used need not be controlled precisely.

Still a further embodiment of the invention is a method of producing a heat shrinkable film comprising the steps of mixing together from about 60% to about 95% by weight of a polyvinylidene chloride copolymer and from about 5% to about 40% by weight of an ethylene vinyl acetate copolymer containing from about 5% to about 18% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigrams per minute, extruding the mixture, and biaxially orienting the extrudate.

Preferably, the film of the invention is a heat shrinkable multilayer film comprising outer layers of ethylene vinyl acetate containing from about 10% to about 15% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigram per minute and a core layer comprising from about 60% to about 95% by weight of a polyvinylidene chloride copolymer and from 5% to about 40% by weight of an ethylene vinyl acetate copolymer containing from about 5% to about 18% by weight of vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigrams per minute. Preferably, the aforementioned multilayer film consists essentially of the three layers.

The invention accordingly comprises the several steps and relation of one or more of such steps with respect to each of the others, all as exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

Generally, the three layer film of the instant invention has an overall thickness of from about 2 to 3 mils and preferably about 2.4 mils. The biaxial orientation can be carried out in accordance with known methods such as the method described in the U.S. Patent No. 3,555,604 to Pahlke. This patent discloses a process in which a polyethylene material defines an isolated bubble maintained by simple nip rollers and the bubble is subjected to heat and radial expansion due to internal pressure near the draw point of the tubing, that is, the point at which the polyethylene material is at or just below its softening point. This process is generally referred to as the "double bubble" method.

Generally, the polyvinylidene chloride copolymer used in the invention comprises at least about 65% by weight polymerized vinylidene chloride and the balance is a polymer of vinyl chloride, acrylonitrile, an acrylate ester such as methyl methacrylate, or the like.

The film of the invention is preferably biaxially oriented, but it can also be a slot cast film or a blown film prepared by conventional methods.

In accordance with conventional practice, it is understood that additives such as stabilizers, plasticizers, and lubricants can be used for producing the film of the invention and it is understood in the specification and the claims that such additives can be present in accordance with conventional practice.

Illustrative non-limiting examples of the practice of the invention are set out below. Numerous other examples can easily be evolved in the light of the guiding principles and teachings contained herein. The examples given herein are intended mainly to illustrate the invention and not in any sense to limit the manner in which the invention can be practiced.

All percentages and parts stated herein are by weight unless otherwise stated.

As used herein, the term "phr" has the conventional meaning of parts per 100 parts of polymer.

The materials described herein have their properties determined in accordance with the following test methods:

Melt Flow—ASTM D-1238
Ethylene vinyl acetate copolymer—Condition E
Polybutylene—Condition E
Polypropylene-ethylene copolymer—Condition L
Density ASTM B-1505.

The following polymers shown in Table 1 are used in the examples:

Table 1

Polymer	*Melt Flow dg/min*	*Density gm/cc*	*Description*
EVA A	0.3		Ethylene vinyl acetate copolymer; 12% by wt vinyl acetate.
EVA B	0.7		Ethylene vinyl acetate copolymer; 18% by wt vinyl acetate.

Table 1 (contd.)

Polymer	*Melt Flow dg/min*	*Density gm/cc*	*Description*
EVA C	0.5		Ethylene vinyl acetate copolymer; 15% by wt vinyl acetate.
EVA D	1.0		Ethylene vinyl acetate copolymer; 12% by wt vinyl acetate.
EVA E	0.6		Ethylene vinyl acetate copolymer; 9% by wt vinyl acetate.
EVA F	0.3		Ethylene vinyl acetate copolymer; 5% by wt vinyl acetate.
P-E A	12.0	0.899	Polypropylene-ethylene copolymer; typically sold commercially as PP9818 by Diamond Shamrock.
P-B A	2.0	0.91	Polybutylene copolymer; typically sold commercially as Witron 1200 by Witco Chemical Co.
Elastomer A			Ethylene-polypropylene copolymer elastomer; typically sold commercially as Vistalon 702 by Exxon Chemical Co.

The following polyvinylidene chloride polymers shown in Table 2 are used in the examples:

Table 2

Polyvinylidene Chloride	*Type and Commercial Designation by Dow Chemical Company*
PVDC A	Emulsion type, Dow 5236.13
PVDC B	Emulsion type; Dow 925
PVDC C	Suspension type; Dow 468
PVDC D	Suspension type; available from Kureha Chemical Co.

The following blends of polyvinylidene chloride copolymers shown in Table 3 are used in the examples:

Table 3

Blend 1	
100 phr	PVDC A
6.75 phr	stabilizer, plasticizer, and lubricant
Blend 2	
100 phr	PVDC A
5.0 phr	stabilizer, plasticizer, and lubricant
Blend 3	
100 phr	PVDC A
3.0 phr	stabilizer and lubricant
Blend 4	
100 phr	PVDC B
6.75 phr	stabilizer, plasticizer, and lubricant
Blend 5	
100 phr	PVDC B
5.75 phr	stabilizer, plasticizer, and lubricant
Blend 6	
100 phr	PVDC B
6.5 phr	stabilizer, plasticizer, and lubricant
Blend 7	
90 phr	PVDC A
10 phr	PVDC C
6.75 phr	stabilizer, plasticizer, and lubricant

Table 3 (contd.)

Blend 8		
	90 phr	PVDC B
	10 phr	PVDC D
	6.5 phr	stabilizer, plasticizer, and lubricant

Examples 1 to 17

Examples 1 to 17 were carried out using an emulsion type polyvinylidene chloride copolymer in a core layer of a three layer film.

The multilayer film consisted essentially of outer layers of ethylene vinyl acetate copolymer and a core layer as shown in Table 4.

The multilayer film was produced by conventional methods in accordance with the "double bubble" process such as described in the U.S. Patent No. 3,555,604 to Pahlke by coextrusion of layers through a multilayer tubular die. Reference is also had to the Canadian Patent No. 982,923 which teaches a multilayer film including outer layers of ethylene vinyl acetate and a core layer of vinylidene chloride copolymer.

For the Examples 4 to 12, and 17, the thicknesses of the layers were not measured. The layers were controlled to maintain thickness about the same as the corresponding layers of the Examples 1 to 3, 15 and 16.

Table 4

Ex.	*First Outer Layer—EVA C % Thickness*	*Second Outer Layer—EVA A % Thickness*	*Core Layer PVDC Blend %*	*Core Layer EVA %*
1	23.1	58.5	Blend 1 95.0	EVA C 5.0
2	24.3	54.5	Blend 2 94.0	EVA B 6.0
3	24.5	57.1	Blend 3 90.0	EVA B 10.0
4			Blend 4 94.0	EVA A 6.0
5			Blend 4 90.0	EVA A 10.0
6			Blend 4 85.0	EVA A 15.0
7			Blend 4 80.0	EVA A 20.0
8			Blend 4 100.0	—
9			Blend 5 94.0	EVA A 6.0
10			Blend 5 90.0	EVA A 10.0
11			Blend 5 85.0	EVA A 15.0
12			Blend 5 80.0	EVA A 20.0
13	25.0	54.0	Blend 6 100.0	—
14	24.6	55.0	Blend 6 90.0	EVA A 10.0
15	24.1	54.6	Blend 6 65.0	EVA A 35.0
16	25.4	53.3	Blend 6 50.0	EVA A 50.0
17			Blend 6 40.0	EVA A 60.0

EVA=ethylene vinyl acetate copolymer.
Total film thickness is about 2.5 mils.

Examples 18 to 37

Examples 18 to 37 were carried out by the same method as the Examples 1 to 17 and used a blend of emulsion and suspension types of polyvinylidene chloride polymer. Table 5 shows the examples 18 to 37.

The thicknesses of the layers of the Examples 33 to 37 were controlled to be about the same as the corresponding layers of the Examples 18 to 32.

Examples 38 and 39

Examples 38 and 39 were carried out by the same method as the Examples 1 to 17 except that the Example 39 had four layers. Table 6 shows the Examples 38 and 39. For the Examples 38, the first outer layer was EVA C and for the Example 39 the first outer layer was a blend of 40% by weight of P-E A, 40% by weight of P-B A and 20% by weight of Elastomer A.

Table 5

	First Outer Layer—EVA C	*Second Outer Layer—EVA A*	*Core Layer*	
Ex.	*% Thickness*	*% Thickness*	*PVDC Blend %*	*EVA %*
18	25.5	57.9	Blend 7 95	EVA B 5
19	24.2	54.9	Blend 8 94	EVA B 6
20	24.2	54.9	Blend 8 94	EVA C 6
21	24.2	54.9	Blend 8 94	EVA A 6
22	24.6	55.3	Blend 8 100	—
22	23.8	54.6	Blend 8 92	EVA B 8
24	23.8	54.6	Blend 8 90	EVA B 10
25	23.8	54.6	Blend 8 92	EVA C 8
26	23.9	54.6	Blend 8 90	EVA C 10
27	24.0	55.1	Blend 8 92	EVA A 8
28	25.1	54.1	Blend 8 90	EVA A 10
29	25.1	54.1	Blend 8 88	EVA A 12
30	23.7	54.6	Blend 8 85	EVA A 15
31	23.7	54.6	Blend 8 80	EVA A 20
32	23.4	55.0	Blend 8 85	EVA C 15
33			Blend 8 70	EVA A 30
34			Blend 8 60	EVA A 40
35			Blend 8 90	EVA D 10
36			Blend 8 90	EVA E 10
37			Blend 8 90	EVA F 10

EVA=ethylene vinyl acetate copolymer.
Total film thickness is about 2.5 mils.

Table 6

	First Outer Layer	*Second Outer Layer—EVA A*	*First Core Layer—EVA*	*Second Core Layer*	
Ex.	*% Thickness*	*% Thickness*	*% Thickness*	*PVDC Blend %*	*EVA %*
38	25.2	54.2	—	Blend 7 95	EVA B 5
39	23.9	41.5	EVA C 11.2	Blend 7 95	EVA B 5

EVA=ethylene vinyl acetate copolymer.
Total film thickness is about 3 mils.

Test Results

The films of the three sets of examples, that is, Examples 1 to 17, 18 to 37, 38 and 39 were tested for various properties and the results of these tests are given in the Tables 7, 8, 9. For some examples, some of the parameters were not measured and consequently, are not shown.

Several bags were formed by conventional methods from various films and found to be satisfactory.

Table 7

Ex.	Haze	Gloss	Tensile Strength M psi	% Elongation at break	Secant Modulus RT M psi	Secant Modulus 30°F M psi	% Shrink 80°C	% Shrink 90°C	% Shrink 100°C	Shrink Force 90°C grams/mil	Shrink Force RT grams/mil	O_2 Transmission Total cm^3 100 in^2-24 hrs-atm	O_2 Transmission Per Mil cm^3-mil 100 in^2-24 hrs-atm	Elmendorf Tear gm/l/1000 in
1	4.8	85.5	7.9	233	16.9	60.8	19	41	58	96.8	27.7	2.55	5.99	24
			8.5	212	17.1	60.7	26	51	60	115.3	44.4			26
2	4.8	84.4	8.2	239	23.7	72.6	24	40	44	90.8	30.2	0.83	2.05	37
			9.7	189	21.8	79.8	31	52	55	132.8	48.1			29
3	6.2	84.5	8.2	264	22.8	83.0	22	45	49	81.1	23.6	<0.5	—	38
			9.6	193	21.9	83.2	30	54	58	126.3	37.1			64
4	14.8	79.0				71.2		46				1.85	5.00	
						71.0		52						
5	11.5	78.0				74.0		47				1.82	5.10	
						73.6		53						
6	12.8	80.0				75.0		46				1.75	4.63	
						76.8		53						
7	7.5	83.0				70.1		47				2.01	5.65	
						65.9		55						
8	3.6	87.0				81.0		46				2.10	5.61	
						80.0		53						
9	12.0	80.0				74.7		47				1.60	4.40	
						76.7		53						
10	9.7	78.0				74.6		44				1.75	4.64	
						73.9		52						
11	9.4	79.0				77.5		46				1.31	3.46	
						75.3		53						
12	8.8	84.0				68.2		51				1.53	4.23	
						66.2		60						
13	1.7	90.1				68.9		49		108.7	23.1			39
						68.5		54		25.5	26.8			36
14	7.5	84.6				72.9		47		88.7	26.3			36
						74.4		52		106.1	34.5			31
15	3.4	95.6				53.8		57		106.7	28.0			25
						52.2		58		128.9	32.2			19
16	3.9	95.1				42.9		51		86.3	19.5			30
						40.4		59		145.7	41.8			19
17	4.7	91.3				36.1		54		95.3	21.2			22
						32.4		59		122.4	29.5			17

Table 8

Sample	Haze	Gloss	Tensile Strength M psi	% Elongation at break	Secant Modulus RT M psi	Secant Modulus +30°F M psi	% Shrink 80°C	% Shrink 90°C	% Shrink 100°C	Shrink Force 90°C grams/mil	Shrink Force RT grams/mil	O_2 Transmission Total cm^3 100 in-24 hrs-atm	O_2 Transmission Per Mil cm^3-mil 100 in^2-24 hrs-atm	Elmendorf Tear gm/l/1000 in
18	5.1	84.3	7.5	223	21.2	73.3	24	43	48	97.1	31.3	0.86	2.10	31
			8.5	196	20.9	79.9	31	51	58	123.3	40.2			23
19	5.6	83.8	6.6	276	29.5	61.6	23	47	53	75.2	19.0	1.33	3.82	41
			7.6	215	26.6	64.9	33	54	59	115.9	33.3			37
20	7.5	81.1	6.6	262	28.5	65.8	24	44	50	78.4	24.8	1.59	4.22	41
			7.4	216	26.0	66.9	32	52	56	122.2	39.2			31
21	8.8	82.3	7.4	251	23.3	61.0	23	43	54	90.4	26.9	1.55	4.40	40
			6.8	217	22.9	63.0	33	51	56	116.9	38.1			34
22	8.6	80.2	6.6	245	25.9	64.5	27	48	54	87.3	24.6	2.17		43
			7.2	203	22.7	64.8	34	52	58	107.8	27.1			36
23	2.6	85.8	6.9	239	25.2	72.2	24	46	54	91.9	25.3	1.47	4.16	38
			7.6	203	25.0	74.2	33	51	58	120.3	37.3			32
24	5.8	86.2	7.2	235	22.0	60.7	22	50	58	91.8	21.9	2.13	5.62	33
			7.5	211	20.4	65.9	32	58	62	114.5	31.2			28
25	6.3	81.6	6.9	272	23.9	68.8	20	43	53	83.3	24.2	1.88	4.74	39
			7.4	211	23.1	68.4	31	53	58	117.9	19.1			35
26	5.6	82.4	6.8	266	22.7	56.7	21	47	54	84.9	24.3	2.15	5.67	38
			7.6	232	21.3	64.0	31	53	60	109.3	35.2			32
27	6.9	80.2	6.0	276	22.3	68.9	19	48	56	68.4	27.8	2.53	6.13	45
			7.1	229	21.1	72.3	30	54	62	102.7	30.1			33
28	13.4	77.5	6.4	253	23.2	77.8	24	48	56	88.5	24.4	2.02	5.45	39
			7.4	205	22.0	65.0	33	55	60	125.0	38.6			29
29	13.9	77.0	6.6	254	22.2	68.8	24	49	54	91.5	27.9	2.14	5.97	38
			7.6	214	20.9	61.9	33	55	62	127.9	40.5			29
30	8.2	87.2	6.6	251	20.0	62.3	27	54	60	89.1	23.4	3.37	9.32	36
			7.1	190	18.8	57.5	36	61	67	129.2	33.2			27
31	5.5	83.6	6.9	279	23.2	67.2	25	50	57	84.0	21.6	2.84	8.01	35
			7.9	225	20.8	66.0	34	60	63	119.6	33.9			27
32	7.5	82.2	6.6	286	22.4	70.4	22	48	56	83.1	22.9	2.23	5.98	34
			7.4	209	20.8	64.2	31	58	63	122.8	38.3			31
33	6.4	79.0	6.8	257	19.5	71.2	24	46	61	103.8	28.8	1.85	5.00	35
			7.2	237	17.7	71.0	33	52	66	120.7	41.3			31
34	5.8	78.0	7.3	254	17.3	74.0	23	47	66	97.7	24.3	1.82	5.10	31
			7.2	227	16.0	73.6	33	53	68	118.9	40.7			29
35	9.8	80.0	6.9	265	21.1	75.0	26	46	50	94.6	33.6	1.75	4.61	38
			7.6	223	19.4	76.8	35	53	54	126.9	45.1			29

Table 8 (continued)

Sample	Haze	Gloss	Tensile Strength M psi	% Elongation at break	Secant Modulus RT M psi	Secant Modulus +30°F M psi	% Shrink 80°C	% Shrink 90°C	% Shrink 100°C	Shrink Force 90°C grams/mil	Shrink Force RT grams/mil	O_2 Transmission Total cm^3 100 in^2-24 hrs-atm	O_2 Transmission Per Mil cm^3-mil 100 in^2-24 hrs-atm	Elmendorf Tear gm/l/1000 in
36	14.4	83.0	6.6	261	22.4	70.1	24	47	50	86.8	31.4	2.01	5.65	37
			7.0	211	20.4	65.9	32	55	57	119.8	46.3			32
37	14.0	87.0	6.9	267	19.9	81.0	22	46	51	100.8	36.2	2.10	5.61	25
			6.8	204	18.9	80.0	30	53	60	125.8	49.8			25

Table 9

Ex.	Haze	Gloss	Tensile Strength M psi	% Elongation at break	Secant Modulus RT M psi	Secant Modulus +30°F M psi	% Shrink 80°C	% Shrink 90°C	% Shrink 100°C	Shrink Force 90°C grams/mil	Shrink Force RT grams/mil	O_2 Transmission Total cm^3 100 in^2-24 hrs-atm	Elmendorf Tear gm/l/1000 in
38	6.6	84.1	7.7	276	24.3	72.7	22	39	54	75.7	22.6	0.93	39
			8.9	222	22.2	72.3	31	49	56	122.3	35.3		31
39	6.9	71.8	9.1	160	33.5	107.6	22	34	37	96.3	48.6	0.98	16
			8.5	115	32.1	113.6	25	39	45	111.6	54.8		19

The examples surprisingly show that blends of the polyvinylidene chloride copolymer and ethylene vinyl acetate copolymer of the invention provide acceptable levels of permeability for use in connection with the storage of foodstuff.

Typically, a three layer film including a core layer of a blend of the invention having from about 5% to about 20% by weight ethylene vinyl acetate copolymer containing from about 5% to about 15% by weight vinyl acetate has total oxygen permeability at room temperature of less than about 3 cubic centimeter per 100 square inches-24 hours-atmosphere.

A three layer film including a core layer of a blend of the invention having about 10% by weight ethylene vinyl acetate copolymer containing from about 5% to about 18% by weight vinyl acetate exhibits a total oxygen permeability at room temperature of about 2.3 cubic centimeter per 100 square inches-24 hours-atmosphere.

A three layer film including a core layer of a blend of the invention having from about 5% to about 40% by weight ethylene vinyl acetate copolymer containing about 12% by weight vinyl acetate exhibits a total oxygen permeability at room temperature of about 2.4 cubic centimeter per 100 square inches-24 hours-atmosphere.

The oxygen permeability of the multilayered films is determined by the polyvinylidene chloride copolymer and ethylene vinyl acetate copolymer layer.

We wish it to be understood that we do not desire to be limited to the exact details of construction shown and described, for obvious modifications will occur to a person skilled in the art.

Having thus described the invention, what we claim as new and desire to be secured by Letters Patent, is as follows:

Claims

1. A film comprising from about 60% to about 95% by weight of a polyvinylidene chloride copolymer and from about 5% to about 40% by weight of an ethylene vinyl acetate copolymer containing from about 5% to about 18% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigram per minute.

2. A film as claimed in Claim 1, wherein said ethylene vinyl acetate copolymer contains from about 5% to about 15% by weight vinyl acetate.

3. A film as claimed in Claim 1 or 2, wherein said polyvinylidene chloride copolymer is from about 80% to about 95% by weight and said ethylene vinyl acetate copolymer is from 5% to about 20% by weight.

4. A film as claimed in any one of the preceding claims, wherein said polyvinylidene chloride copolymer is about 90% by weight and said ethylene vinyl acetate copolymer is about 10% by weight.

5. A film as claimed in any one of the preceding claims, wherein said ethylene vinyl acetate copolymer contains about 12% by weight vinyl acetate.

6. A film as claimed in any one of the preceding claims, wherein said polyvinylidene chloride copolymer is an emulsion type.

7. A film as claimed in any one of Claims 1 to 5, wherein said polyvinylidene chloride copolymer is a suspension type.

8. A film as claimed in any one of Claims 1 to 5, wherein said polyvinylidene chloride copolymer is a blend of emulsion and suspension types.

9. A film as claimed in any one of the preceding claims, wherein said film is biaxially oriented.

10. A film as claimed in any one of Claims 1 to 9, wherein said film is a slot cast film.

11. A film as claimed in any one of Claims 1 to 9, wherein said film is a blown film.

12. A film as claimed in any one of the preceding claims, which is a multilayer film having coextruded layers.

13. A film as claimed in any one of Claims 1 to 11, further comprising outer layers of ethylene vinyl acetate copolymer containing from about 10% to about 15% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigram per minute.

14. A film as claimed in Claim 13, consisting essentially of the outer and core layers.

15. A film as claimed in Claim 13 or 14, wherein the overall thickness is from about 2 to about 3 mils.

16. A method of producing a film comprising the steps of mixing together from about 60% to about 95% by weight of a polyvinylidene chloride copolymer and from about 5% to about 40% by weight of an ethylene vinyl acetate copolymer containing from about 5% to about 18% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigram per minute; and extruding the mixture to form said film.

17. A method as claimed in Claim 16, wherein said ethylene vinyl acetate copolymer contains from about 5% to about 15% by weight vinyl acetate.

18. A method as claimed in Claim 16 or 17, wherein said polyvinylidene chloride copolymer is from about 80% to about 95% by weight and said ethylene vinyl acetate copolymer is from 5% to about 20% by weight.

19. A method as claimed in any one of Claims 16 to 18, wherein said polyvinylidene chloride copolymer is about 90% by weight and said ethylene vinyl acetate copolymer is about 10% by weight.

20. A method as claimed in any one of Claims 16 to 19, wherein said ethylene vinyl acetate copolymer contains about 12% by weight vinyl acetate.

21. A method as claimed in any one of Claims 16 to 20, wherein said polyvinylidene chloride copolymer is an emulsion type.

22. A method as claimed in any one of Claims 16 to 20, wherein said polyvinylidene chloride copolymer is a suspension type.

23. A method as claimed in any one of Claims 16 to 20, wherein said polyvinylidene chloride copolymer is a blend of emulsion and suspension types.

24. A method as claimed in any one of Claims 16 to 23, further comprising the step of biaxially orienting said film.

25. A method as claimed in any one of Claims 16 to 24, wherein said film is formed by the slot cast method.

26. A method as claimed in any one of Claims 16 to 24, further comprising the step of forming a blown film.

27. A method as claimed in any one of the preceding claims, wherein said film is a multilayer film and the layers of said film are coextruded.

28. A method as claimed in Claim 27, wherein the outer layers of said film are ethylene vinyl acetate copolymer containing from about 10% to about 15% by weight vinyl acetate and having a melt flow of from about 0.1 to about 1.0 decigram per minute.

29. A method as claimed in Claim 28, consisting essentially of the outer and core layers.

30. A method as claimed in any one of Claims 27 to 29, wherein the overall thickness is from about 2 to about 3 mils.

31. A film as claimed in Claim 1, substantially as hereinbefore described in any one of the foregoing Examples.

32. A method for producing a film substantially as hereinbefore described in any one of the foregoing Examples.

33. A bag made from a film as claimed in any one of Claims 1 to 15 or 31.

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